

## **POLY(HYDRAZONE)-BASED CHARGE TRANSPORT MATERIALS**

### **5 FIELD OF THE INVENTION**

This invention relates to organophotoreceptors suitable for use in electrophotography and, more specifically, to organophotoreceptors including a charge transport material comprising a polymer having repeating hydrazone groups. Furthermore, the invention further relates to a method for forming a charge transport material comprising a polymer having repeating hydrazone groups.

### **BACKGROUND OF THE INVENTION**

In electrophotography, an organophotoreceptor in the form of a plate, disk, sheet, belt, drum or the like having an electrically insulating photoconductive element on an electrically conductive substrate is imaged by first uniformly electrostatically charging the surface of the photoconductive layer, and then exposing the charged surface to a pattern of light. The light exposure selectively dissipates the charge in the illuminated areas where light strikes the surface, thereby forming a pattern of charged and uncharged areas, referred to as a latent image. A liquid or solid toner is then provided in the vicinity of the latent image, and toner droplets or particles deposit in the vicinity of either the charged or uncharged areas to create a toned image on the surface of the photoconductive layer. The resulting toned image can be transferred to a suitable ultimate or intermediate receiving surface, such as paper, or the photoconductive layer can operate as an ultimate receptor for the image. The imaging process can be repeated many times to complete a single image, for example, by overlaying images of distinct color components or effect shadow images, such as overlaying images of distinct colors to form a full color final image, and/or to reproduce additional images.

Both single layer and multilayer photoconductive elements have been used. In single layer embodiments, a charge transport material and charge generating material are combined with a polymeric binder and then deposited on the electrically conductive substrate. In multilayer embodiments, the charge transport material and charge

generating material are present in the element in separate layers, each of which can optionally be combined with a polymeric binder, deposited on the electrically conductive substrate. Two arrangements are possible for a two-layer photoconductive element. In one two-layer arrangement (the "dual layer" arrangement), the charge-generating layer is deposited on the electrically conductive substrate and the charge transport layer is deposited on top of the charge generating layer. In an alternate two-layer arrangement (the "inverted dual layer" arrangement), the order of the charge transport layer and charge generating layer is reversed.

In both the single and multilayer photoconductive elements, the purpose of the charge generating material is to generate charge carriers (i.e., holes and/or electrons) upon exposure to light. The purpose of the charge transport material is to accept at least one type of these charge carriers and transport them through the charge transport layer in order to facilitate discharge of a surface charge on the photoconductive element. The charge transport material can be a charge transport compound, an electron transport compound, or a combination of both. When a charge transport compound is used, the charge transport compound accepts the hole carriers and transports them through the layer with the charge transport compound. When an electron transport compound is used, the electron transport compound accepts the electron carriers and transports them through the layer with the electron transport compound.

Organophotoreceptors may be used for both dry and liquid electrophotography. There are many differences between dry and liquid electrophotography. A significant difference is that a dry toner is used in dry electrophotography, whereas a liquid toner is used in liquid electrophotography. A potential advantage of liquid electrophotography is that it can provide a higher resolution and thus sharper images than dry electrophotography because liquid toner particles can be generally significantly smaller than dry toner particles. As a result of their smaller size, liquid toners are able to provide images of higher optical density than dry toners.

In both dry and liquid electrophotography, the charge transport material used for the organophotoreceptor should be compatible with the polymeric binder in the photoconductive element. The selection of a suitable polymeric binder for a particular charge transport material can place constraints on the formation of the photoconductive

element. If the charge transport material is not compatible with the polymeric binder, the charge transport material may phase-separate or crystallize in the polymeric binder matrix, or may diffuse onto the surface of the layer containing the charge transport material. If such incompatibility occurs, the organophotoreceptor can cease to transport charges.

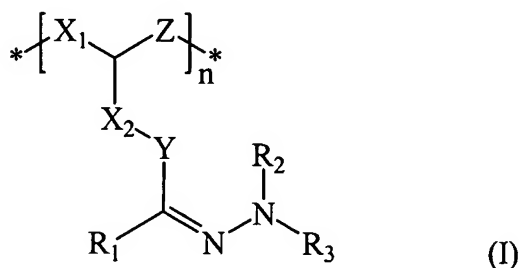
Furthermore, liquid electrophotography faces an additional issue. In particular, the organophotoreceptor for liquid electrophotography is in contact with the liquid carrier of a liquid toner while the toner dries or pending transfer to a receiving surface. As a result, the charge transport material in the photoconductive element may be removed by extraction by the liquid carrier. Over a long period of operation, the amount of the charge transport material removed by extraction may be significant and, therefore, detrimental to the performance of the organophotoreceptor.

### SUMMARY OF THE INVENTION

This invention provides organophotoreceptors having good electrostatic properties such as high  $V_{acc}$  and low  $V_{dis}$ . This invention also provides charge transport materials having reduced extraction by liquid carriers and reducing the need for a polymeric binder.

In a first aspect, an organophotoreceptor comprises an electrically conductive substrate and a photoconductive element on the electrically conductive substrate, the photoconductive element comprising:

(a) a charge transport material comprising a polymer having the formula:



where  $X_1$  and  $X_2$  are, each independently, a bond or a linking group, such as  $-(CH_2)_m-$  group, where  $m$  is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, an  $NR_a$  group, a  $CR_b$  group, a  $CR_cR_d$  group, or a  $SiR_eR_f$  where  $R_a$ ,  $R_b$ ,  $R_c$ ,  $R_d$ ,  $R_e$ , and  $R_f$  are,

each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, an alkyl group, an alkoxy group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups or a benzo group;

5           Y comprises a bond or an arylamine group, such as carbazolyl groups and (N-substituted)arylamine groups;

          Z comprises a bond, O, S, or NR<sub>4</sub>;

          R<sub>1</sub> and R<sub>4</sub> comprise, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group;

10           R<sub>2</sub> and R<sub>3</sub> comprise, each independently, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group; and

          n is a distribution of integers between 1 and 100,000 with an average value of greater than one; and

          (b) a charge generating compound.

15           The asterisks (\*) indicate terminal groups on the polymer, which may vary between different polymer molecules depending on the state of the particular polymerization process at the end of the polymerization step.

          The organophotoreceptor may be provided, for example, in the form of a plate, a flexible belt, a flexible disk, a sheet, a rigid drum, or a sheet around a rigid or compliant  
20           drum. In one embodiment, the organophotoreceptor includes: (a) a photoconductive element comprising the charge transport material, the charge generating compound, a second charge transport material, and a polymeric binder; and (b) the electrically conductive substrate.

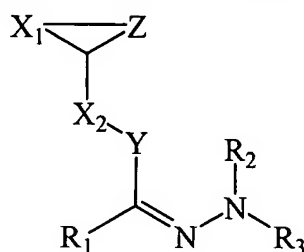
          In a second aspect, the invention features an electrophotographic imaging  
25           apparatus that comprises (a) a light imaging component; and (b) the above-described organophotoreceptor oriented to receive light from the light imaging component. The apparatus can further comprise a toner dispenser, such as a liquid toner dispenser. The method of electrophotographic imaging with photoreceptors containing the above noted charge transport materials is also described.

30           In a third aspect, the invention features an electrophotographic imaging process that includes (a) applying an electrical charge to a surface of the above-described

organophotoreceptor; (b) imagewise exposing the surface of the organophotoreceptor to radiation to dissipate charge in selected areas and thereby form a pattern of at least relatively charged and uncharged areas on the surface; (c) contacting the surface with a toner, such as a liquid toner that includes a dispersion of colorant particles in an organic liquid, to create a toned image; and (d) transferring the toned image to a substrate.

In a fourth aspect, the invention features a charge transport material comprising a polymer having Formula (I) above.

In a fifth aspect, the invention features a method for forming a charge transport material comprising a polymer, the method comprising the step of ring-open polymerizing a charge transport material having the formula:



where  $\text{X}_1$  and  $\text{X}_2$  are, each independently, a bond or a linking group, such as  $-(\text{CH}_2)_m-$  group, where  $m$  is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, an  $\text{NR}_a$  group, a  $\text{CR}_b$  group, a  $\text{CR}_c\text{R}_d$  group, or a  $\text{SiR}_e\text{R}_f$  where  $\text{R}_a$ ,  $\text{R}_b$ ,  $\text{R}_c$ ,  $\text{R}_d$ ,  $\text{R}_e$ , and  $\text{R}_f$  are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, an alkyl group, an alkoxy group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups or a benzo group;

Y comprises a bond or an arylamine group, such as carbazolyl groups and (N-substituted)arylamine groups;

Z comprises a bond, O, S, or  $\text{NR}_4$ ;

$\text{R}_1$  and  $\text{R}_4$  comprise, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group; and

$\text{R}_2$  and  $\text{R}_3$  comprise, each independently, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group.

In a sixth aspect, the invention features a method for forming a charge transport material comprising a polymer, the method comprising the steps of:

- a) reacting a polymer comprising molecules having repeating arylamine groups with an acylating agent to form an aldehyde derivative or a ketone derivative; and
- b) reacting the aldehyde derivative or the ketone derivative with an (N,N-disubstituted)hydrazine.

The invention provides suitable charge transport materials for organophotoreceptors featuring a combination of good mechanical and electrostatic properties. These photoreceptors can be used successfully with liquid toners to produce high quality images. The high quality of the imaging system can be maintained after repeated cycling.

Other features and advantages of the invention will be apparent from the following description of the particular embodiments thereof, and from the claims.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

An organophotoreceptor as described herein has an electrically conductive substrate and a photoconductive element including a charge generating compound and a charge transport material comprising a polymer having repeating hydrazone groups. In some embodiments, the hydrazone groups are arylamine hydrazone groups and each of the arylamine hydrazone groups is linked to the backbone of the polymer through a linking group. These charge transport materials have desirable properties as evidenced by their performance in organophotoreceptors for electrophotography. In particular, the charge transport materials of this invention have high charge carrier mobilities and good compatibility with various binder materials, and possess excellent electrophotographic properties. The organophotoreceptors according to this invention generally have a high photosensitivity, a low residual potential, and a high stability with respect to cycle testing, crystallization, and organophotoreceptor bending and stretching. The organophotoreceptors are particularly useful in laser printers and the like as well as fax machines, photocopiers, scanners and other electronic devices based on electrophotography. The use of these charge transport materials is described in more

detail below in the context of laser printer use, although their application in other devices operating by electrophotography can be generalized from the discussion below.

To produce high quality images, particularly after multiple cycles, it is desirable for the charge transport materials to form a homogeneous solution with the polymeric binder and remain approximately homogeneously distributed through the organophotoreceptor material during the cycling of the material. In addition, it is desirable to increase the amount of charge that the charge transport material can accept (indicated by a parameter known as the acceptance voltage or " $V_{acc}$ "), and to reduce retention of that charge upon discharge (indicated by a parameter known as the discharge voltage or " $V_{dis}$ ").

The charge transport materials may comprise monomeric molecules (e.g., N-ethyl-carbazolo-3-aldehyde-N-methyl-N-phenyl-hydrazone, dimeric molecules (e.g., disclosed in U.S. Patent Nos. 6,140,004 and 6,670,085), or polymeric compositions (e.g., poly(vinylcarbazole)). Furthermore, the charge transport materials can be classified as a charge transport compound or an electron transport compound. There are many charge transport compounds and electron transport compounds known in the art for electrophotography. Non-limiting examples of charge transport compounds include, for example, pyrazoline derivatives, fluorene derivatives, oxadiazole derivatives, stilbene derivatives, enamine derivatives, enamine stilbene derivatives, hydrazone derivatives, carbazole hydrazone derivatives, (N,N-disubstituted)arylamines such as triaryl amines, polyvinyl carbazole, polyvinyl pyrene, polyacenaphthylene, or multi-hydrazone compounds comprising at least two hydrazone groups and at least two groups selected from the group consisting of (N,N-disubstituted)arylamine such as triphenylamine and heterocycles such as carbazole, julolidine, phenothiazine, phenazine, phenoxazine, phenoxathiin, thiazole, oxazole, isoxazole, dibenzo(1,4)dioxin, thianthrene, imidazole, benzothiazole, benzotriazole, benzoxazole, benzimidazole, quinoline, isoquinoline, quinoxaline, indole, indazole, pyrrole, purine, pyridine, pyridazine, pyrimidine, pyrazine, triazole, oxadiazole, tetrazole, thiadiazole, benzisoxazole, benzisothiazole, dibenzofuran, dibenzothiophene, thiophene, thianaphthene, quinazoline, or cinnoline.

Non-limiting examples of electron transport compounds include, for example, bromoaniline, tetracyanoethylene, tetracyanoquinodimethane, 2,4,7-trinitro-9-fluorenone,

2,4,5,7-tetranitro-9-fluorenone, 2,4,5,7-tetranitroxanthone, 2,4,8-trinitrothioxanthone, 2,6,8-trinitro-indeno[1,2-b]thiophene-4-one, and 1,3,7-trinitrodibenzo thiophene-5,5-dioxide, (2,3-diphenyl-1-indenylidene)malononitrile, 4H-thiopyran-1,1-dioxide and its derivatives such as 4-dicyanomethylene-2,6-diphenyl-4H-thiopyran-1,1-dioxide, 4-  
5 dicyanomethylene-2,6-di-m-tolyl-4H-thiopyran-1,1-dioxide, and unsymmetrically substituted 2,6-diaryl-4H-thiopyran-1,1-dioxide such as 4H-1,1-dioxo-2-(p-isopropylphenyl)-6-phenyl-4-(dicyanomethylidene)thiopyran and 4H-1,1-dioxo-2-(p-isopropylphenyl)-6-(2-thienyl)-4-(dicyanomethylidene)thiopyran, derivatives of phospho-2,5-cyclohexadiene, alkoxycarbonyl-9-fluorenylidene)malononitrile derivatives such as  
10 (4-n-butoxycarbonyl-9-fluorenylidene)malononitrile, (4-phenethoxycarbonyl-9-fluorenylidene)malononitrile, (4-carbitoxy-9-fluorenylidene)malononitrile, and diethyl(4-n-butoxycarbonyl-2,7-dinitro-9-fluorenylidene)malonate, anthraquinodimethane derivatives such as 11,11,12,12-tetracyano-2-alkylanthraquinodimethane and 11,11-dicyano-12,12-bis(ethoxycarbonyl)anthraquinodimethane, anthrone derivatives such as 1-  
15 chloro-10-[bis(ethoxycarbonyl)methylene]anthrone, 1,8-dichloro-10-[bis(ethoxy carbonyl) methylene]anthrone, 1,8-dihydroxy-10-[bis(ethoxycarbonyl)methylene] anthrone, and 1-cyano-10-[bis(ethoxycarbonyl)methylene]anthrone, 7-nitro-2-aza-9-fluorenylidene-malononitrile, diphenoquinone derivatives, benzoquinone derivatives, naphthoquinone derivatives, quinine derivatives, tetracyanoethylenecyanoethylene, 2,4,8-  
20 trinitro thioxanthone, dinitrobenzene derivatives, dinitroanthracene derivatives, dinitroacridine derivatives, nitroanthraquinone derivatives, dinitroanthraquinone derivatives, succinic anhydride, maleic anhydride, dibromo maleic anhydride, pyrene derivatives, carbazole derivatives, hydrazone derivatives, N,N-dialkylaniline derivatives, diphenylamine derivatives, triphenylamine derivatives, triphenylmethane derivatives, 25 tetracyano quinodimethane, 2,4,5,7-tetranitro-9-fluorenone, 2,4,7-trinitro-9-dicyanomethylene fluorenone, 2,4,5,7-tetranitroxanthone derivatives, 2,4,8-trinitrothioxanthone derivatives, 1,4,5,8-naphthalene bis-dicarboximide derivatives as described in U.S. Patent Nos. 5,232,800, 4,468,444, and 4,442,193 and phenylazoquinolide derivatives as described in U.S. Patent No. 6,472,514. In some  
30 embodiments of interest, the electron transport compound comprises an (alkoxycarbonyl-



9-fluorenylidene)malononitrile derivative, such as (4-n-butoxycarbonyl-9-fluorenylidene)malononitrile, and 1,4,5,8-naphthalene bis-dicarboximide derivatives.

Although there are many charge transport materials available, there is a need for other charge transport materials to meet the various requirements of particular electrophotography applications.

In electrophotography applications, a charge-generating compound within an organophotoreceptor absorbs light to form electron-hole pairs. These electrons and holes can be transported over an appropriate time frame under a large electric field to discharge locally a surface charge that is generating the field. The discharge of the field at a particular location results in a surface charge pattern that essentially matches the pattern drawn with the light. This charge pattern then can be used to guide toner deposition. The charge transport materials described herein are especially effective at transporting charge, and in particular holes from the electron-hole pairs formed by the charge generating compound. In some embodiments, a specific electron transport compound or charge transport compound can also be used along with the charge transport material of this invention.

The layer or layers of materials containing the charge generating compound and the charge transport materials are within an organophotoreceptor. To print a two dimensional image using the organophotoreceptor, the organophotoreceptor has a two dimensional surface for forming at least a portion of the image. The imaging process then continues by cycling the organophotoreceptor to complete the formation of the entire image and/or for the processing of subsequent images.

The organophotoreceptor may be provided in the form of a plate, a flexible belt, a disk, a rigid drum, a sheet around a rigid or compliant drum, or the like. The charge transport material can be in the same layer as the charge generating compound and/or in a different layer from the charge generating compound. Additional layers can be used also, as described further below.

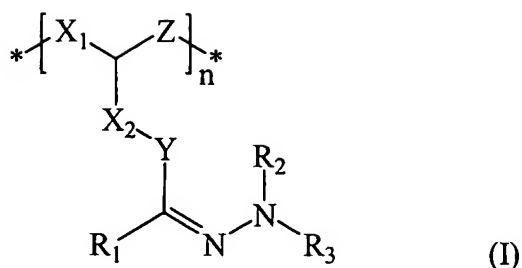
In some embodiments, the organophotoreceptor material comprises, for example: (a) a charge transport layer comprising the charge transport material and a polymeric binder; (b) a charge generating layer comprising the charge generating compound and a polymeric binder; and (c) the electrically conductive substrate. The charge transport

layer may be intermediate between the charge generating layer and the electrically conductive substrate. Alternatively, the charge generating layer may be intermediate between the charge transport layer and the electrically conductive substrate. In further embodiments, the organophotoreceptor material has a single layer with both a charge transport material and a charge generating compound within a polymeric binder.

The organophotoreceptors can be incorporated into an electrophotographic imaging apparatus, such as laser printers. In these devices, an image is formed from physical embodiments and converted to a light image that is scanned onto the organophotoreceptor to form a surface latent image. The surface latent image can be used to attract toner onto the surface of the organophotoreceptor, in which the toner image is the same or the negative of the light image projected onto the organophotoreceptor. The toner can be a liquid toner or a dry toner. The toner is subsequently transferred, from the surface of the organophotoreceptor, to a receiving surface, such as a sheet of paper. After the transfer of the toner, the surface is discharged, and the material is ready to cycle again. The imaging apparatus can further comprise, for example, a plurality of support rollers for transporting a paper receiving medium and/or for movement of the photoreceptor, a light imaging component with suitable optics to form the light image, a light source, such as a laser, a toner source and delivery system and an appropriate control system.

An electrophotographic imaging process generally can comprise (a) applying an electrical charge to a surface of the above-described organophotoreceptor; (b) imagewise exposing the surface of the organophotoreceptor to radiation to dissipate charge in selected areas and thereby form a pattern of charged and uncharged areas on the surface; (c) exposing the surface with a toner, such as a liquid toner that includes a dispersion of colorant particles in an organic liquid to create a toner image, to attract toner to the charged or discharged regions of the organophotoreceptor; and (d) transferring the toner image to a substrate.

As described herein, an organophotoreceptor comprises a charge transport material comprising a polymer having the formula:



where  $X_1$  and  $X_2$  are, each independently, a bond or a linking group, such as  $-(CH_2)_m-$  group, where  $m$  is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, an

5  $NR_a$  group, a  $CR_b$  group, a  $CR_cR_d$  group, or a  $SiR_eR_f$  where  $R_a$ ,  $R_b$ ,  $R_c$ ,  $R_d$ ,  $R_e$ , and  $R_f$  are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, an alkyl group, an alkoxy group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups or a benzo group;

10 Y comprises a bond or an arylamine group, such as carbazolyl groups and (N-substituted)arylamine groups;

Z comprises a bond, O, S, or  $NR_4$ ;

$R_1$  and  $R_4$  comprise, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group;

15  $R_2$  and  $R_3$  comprise, each independently, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group; and

$n$  is a distribution of integers between 1 and 100,000 with an average value of greater than one.

A heterocyclic group includes any monocyclic or polycyclic (e.g., bicyclic, 20 tricyclic, etc.) ring compound having at least a heteroatom (e.g., O, S, N, P, B, Si, etc.) in the ring.

An aromatic group can be any conjugated ring system containing  $4n + 2$  pi-electrons. There are many criteria available for determining aromaticity. A widely employed criterion for the quantitative assessment of aromaticity is the resonance energy.

25 Specifically, an aromatic group has a resonance energy. In some embodiments, the resonance energy of the aromatic group is at least 10 KJ/mol. In further embodiments, the resonance energy of the aromatic group is greater than 0.1 KJ/mol. Aromatic groups may

be classified as an aromatic heterocyclic group which contains at least a heteroatom in the  $4n + 2$  pi-electron ring, or as an aryl group which does not contain a heteroatom in the  $4n + 2$  pi-electron ring. The aromatic group may comprise a combination of aromatic heterocyclic group and aryl group. Nonetheless, either the aromatic heterocyclic or the aryl group may have at least one heteroatom in a substituent attached to the  $4n + 2$  pi-electron ring. Furthermore, either the aromatic heterocyclic or the aryl group may comprise a monocyclic or polycyclic (such as bicyclic, tricyclic, etc.) ring.

Non-limiting examples of the aromatic heterocyclic group are furanyl, thiophenyl, pyrrolyl, indolyl, carbazoyl, benzofuranyl, benzothiophenyl, dibenzofuranyl, dibenzothiophenyl, pyridinyl, pyridazinyl, pyrimidinyl, pyrazinyl, triazinyl, tetrazinyl, petazinyl, quinolinyl, isoquinolinyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, naphthyridinyl, pteridinyl, acridinyl, phenanthridinyl, phenanthrolinyl, anthyridinyl, purinyl, pteridinyl, alloxazinyl, phenazinyl, phenothiazinyl, phenoxazinyl, phenoxathiinyl, dibenzo(1,4)dioxinyl, thianthrenyl, and a combination thereof. The aromatic heterocyclic group may also include any combination of the above aromatic heterocyclic groups bonded together either by a bond (as in bicarbazoyl) or by a linking group (as in 1,6 di(10H-10-phenothiazinyl)hexane). The linking group may include an aliphatic group, an aromatic group, a heterocyclic group, or a combination thereof. Furthermore, either an aliphatic group or an aromatic group within a linking group may comprise at least one heteroatom such as O, S, Si, and N.

Non-limiting examples of the aryl group are phenyl, naphthyl, benzyl, or tolanyl group, sexiphenylene, phenanthrenyl, anthracenyl, coronenyl, and tolanylphenyl. The aryl group may also include any combination of the above aryl groups bonded together either by a bond (as in biphenyl group) or a linking group (as in stilbenyl, diphenyl sulfone, an arylamine group). The linking group may include an aliphatic group, an aromatic group, a heterocyclic group, or a combination thereof. Furthermore, either an aliphatic group or an aromatic group within a linking group may comprise at least one heteroatom such as O, S, Si, and N.

Substitution is liberally allowed on the chemical groups to affect various physical effects on the properties of the compounds, such as mobility, sensitivity, solubility, stability, and the like, as is known generally in the art. In the description of chemical

substituents, there are certain practices common to the art that are reflected in the use of language. The term group indicates that the generically recited chemical entity (e.g., alkyl group, phenyl group, aromatic group, arylamine group, julolidine group, carbazole group, (N,N-disubstituted)arylamine group, etc.) may have any substituent thereon which is consistent with the bond structure of that group. For example, where the term 'alkyl group' is used, that term would not only include unsubstituted linear, branched and cyclic alkyls, such as methyl, ethyl, isopropyl, tert-butyl, cyclohexyl, dodecyl and the like, but also substituents having heteroatom, such as 3-ethoxylpropyl, 4-(N,N-diethylamino)butyl, 3-hydroxypentyl, 2-thiolhexyl, 1,2,3-tribromopropyl, and the like, and aromatic group, such as phenyl, naphthyl, carbazolyl, pyrrole, and the like. However, as is consistent with such nomenclature, no substitution would be included within the term that would alter the fundamental bond structure of the underlying group. For example, where a phenyl group is recited, substitution such as 2- or 4-aminophenyl, 2- or 4-(N,N-disubstituted)aminophenyl, 2,4-dihydroxyphenyl, 2,4,6-trithiophenyl, 2,4,6-trimethoxyphenyl and the like would be acceptable within the terminology, while substitution of 1,1,2,2,3,3-hexamethylphenyl would not be acceptable as that substitution would require the ring bond structure of the phenyl group to be altered to a non-aromatic form. Similarly, when referring to arylamine group, the compound or substituent cited includes any substitution that does not substantively alter the chemical nature of the arylamine group in the formula. Where the term moiety is used, such as alkyl moiety or phenyl moiety, that terminology indicates that the chemical material is not substituted. Where the term alkyl moiety is used, that term represents only an unsubstituted alkyl hydrocarbon group, whether branched, straight chain, or cyclic.

## 25 Organophotoreceptors

The organophotoreceptor may be, for example, in the form of a plate, a sheet, a flexible belt, a disk, a rigid drum, or a sheet around a rigid or compliant drum, with flexible belts and rigid drums generally being used in commercial embodiments. The organophotoreceptor may comprise, for example, an electrically conductive substrate and on the electrically conductive substrate a photoconductive element in the form of one or more layers. The photoconductive element can comprise both a charge transport material

and a charge generating compound in a polymeric binder, which may or may not be in the same layer, as well as a second charge transport material such as a charge transport compound or an electron transport compound in some embodiments. For example, the charge transport material and the charge generating compound can be in a single layer.

5 In other embodiments, however, the photoconductive element comprises a bilayer construction featuring a charge generating layer and a separate charge transport layer. The charge generating layer may be located intermediate between the electrically conductive substrate and the charge transport layer. Alternatively, the photoconductive element may have a structure in which the charge transport layer is intermediate between  
10 the electrically conductive substrate and the charge generating layer.

The electrically conductive substrate may be flexible, for example in the form of a flexible web or a belt, or inflexible, for example in the form of a drum. A drum can have a hollow cylindrical structure that provides for attachment of the drum to a drive that rotates the drum during the imaging process. Typically, a flexible electrically conductive  
15 substrate comprises an electrically insulating substrate and a thin layer of electrically conductive material onto which the photoconductive material is applied.

The electrically insulating substrate may be paper or a film forming polymer such as polyester (e.g., polyethylene terephthalate or polyethylene naphthalate), polyimide, polysulfone, polypropylene, nylon, polyester, polycarbonate, polyvinyl resin, polyvinyl  
20 fluoride, polystyrene and the like. Specific examples of polymers for supporting substrates included, for example, polyethersulfone (STABAR<sup>TM</sup> S-100, available from ICI), polyvinyl fluoride (Tedlar<sup>®</sup>, available from E.I. DuPont de Nemours & Company), polybisphenol-A polycarbonate (MAKROFOL<sup>TM</sup>, available from Mobay Chemical Company) and amorphous polyethylene terephthalate (MELINAR<sup>TM</sup>, available from ICI  
25 Americas, Inc.). The electrically conductive materials may be graphite, dispersed carbon black, iodine, conductive polymers such as polypyrroles and Calgon<sup>®</sup> conductive polymer 261 (commercially available from Calgon Corporation, Inc., Pittsburgh, Pa.), metals such as aluminum, titanium, chromium, brass, gold, copper, palladium, nickel, or stainless steel, or metal oxide such as tin oxide or indium oxide. In embodiments of  
30 particular interest, the electrically conductive material is aluminum. Generally, the photoconductor substrate has a thickness adequate to provide the required mechanical

stability. For example, flexible web substrates generally have a thickness from about 0.01 to about 1 mm, while drum substrates generally have a thickness from about 0.5 mm to about 2 mm.

The charge generating compound is a material that is capable of absorbing light to generate charge carriers (such as a dye or pigment). Non-limiting examples of suitable charge generating compounds include, for example, metal-free phthalocyanines (e.g., ELA 8034 metal-free phthalocyanine available from H.W. Sands, Inc. or Sanyo Color Works, Ltd., CGM-X01), metal phthalocyanines such as titanium phthalocyanine, copper phthalocyanine, oxytitanium phthalocyanine (also referred to as titanyl oxyphthalocyanine, and including any crystalline phase or mixtures of crystalline phases that can act as a charge generating compound), hydroxygallium phthalocyanine, squarylium dyes and pigments, hydroxy-substituted squarylium pigments, perylimides, polynuclear quinones available from Allied Chemical Corporation under the trade name INDOFAST™ Double Scarlet, INDOFAST™ Violet Lake B, INDOFAST™ Brilliant Scarlet and INDOFAST™ Orange, quinacridones available from DuPont under the trade name MONASTRAL™ Red, MONASTRAL™ Violet and MONASTRAL™ Red Y, naphthalene 1,4,5,8-tetracarboxylic acid derived pigments including the perinones, tetrabenzoporphyrins and tetranaphthaloporphyrins, indigo- and thioindigo dyes, benzothioxanthene-derivatives, perylene 3,4,9,10-tetracarboxylic acid derived pigments, polyazo-pigments including bisazo-, trisazo- and tetrakisazo-pigments, polymethine dyes, dyes containing quinazoline groups, tertiary amines, amorphous selenium, selenium alloys such as selenium-tellurium, selenium-tellurium-arsenic and selenium-arsenic, cadmium sulphoselenide, cadmium selenide, cadmium sulphide, and mixtures thereof. For some embodiments, the charge generating compound comprises oxytitanium phthalocyanine (e.g., any phase thereof), hydroxygallium phthalocyanine or a combination thereof.

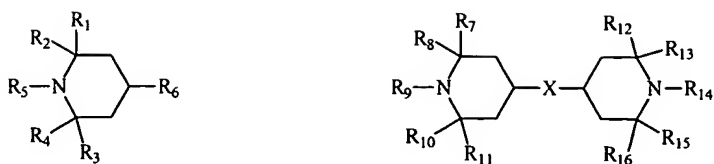
The photoconductive layer of this invention may optionally contain a second charge transport material which may be a charge transport compound, an electron transport compound, or a combination of both. Generally, any charge transport compound or electron transport compound known in the art can be used as the second charge transport material.

An electron transport compound and a UV light stabilizer can have a synergistic relationship for providing desired electron flow within the photoconductor. The presence of the UV light stabilizers alters the electron transport properties of the electron transport compounds to improve the electron transporting properties of the composite. UV light stabilizers can be ultraviolet light absorbers or ultraviolet light inhibitors that trap free radicals.

UV light absorbers can absorb ultraviolet radiation and dissipate it as heat. UV light inhibitors are thought to trap free radicals generated by the ultraviolet light and after trapping of the free radicals, subsequently to regenerate active stabilizer moieties with energy dissipation. In view of the synergistic relationship of the UV stabilizers with electron transport compounds, the particular advantages of the UV stabilizers may not be their UV stabilizing abilities, although the UV stabilizing ability may be further advantageous in reducing degradation of the organophotoreceptor over time. The improved synergistic performance of organophotoreceptors with layers comprising both an electron transport compound and a UV stabilizer are described further in copending U.S. Patent Application Serial Number 10/425,333 filed on April 28, 2003 to Zhu, entitled "Organophotoreceptor With A Light Stabilizer," incorporated herein by reference.

Non-limiting examples of suitable light stabilizer include, for example, hindered trialkylamines such as Tinuvin 144 and Tinuvin 292 (from Ciba Specialty Chemicals, Terrytown, NY), hindered alkoxydialkylamines such as Tinuvin 123 (from Ciba Specialty Chemicals), benzotriazoles such as Tinuvin 328, Tinuvin 900 and Tinuvin 928 (from Ciba Specialty Chemicals), benzophenones such as Sanduvor 3041 (from Clariant Corp., Charlotte, N.C.), nickel compounds such as Arbestab (from Robinson Brothers Ltd, West Midlands, Great Britain), salicylates, cyanocinnamates, benzylidene malonates, benzoates, oxanilides such as Sanduvor VSU (from Clariant Corp., Charlotte, N.C.), triazines such as Cyagard UV-1164 (from Cytec Industries Inc., N.J.), polymeric sterically hindered amines such as Luchem (from Atochem North America, Buffalo, NY). In some embodiments, the light stabilizer is selected from the group consisting of hindered trialkylamines having the following formula:





where  $R_1, R_2, R_3, R_4, R_6, R_7, R_8, R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, R_{15}$  are, each independently, hydrogen, alkyl group, or ester, or ether group; and  $R_5, R_9$ , and  $R_{14}$  are, each independently, alkyl group; and  $X$  is a linking group selected from the group consisting of  $-O-CO-(CH_2)_m-CO-O-$  where  $m$  is between 2 to 20.

The binder generally is capable of dispersing or dissolving the charge transport material (in the case of the charge transport layer or a single layer construction), the charge generating compound (in the case of the charge generating layer or a single layer construction) and/or an electron transport compound for appropriate embodiments.

Examples of suitable binders for both the charge generating layer and charge transport layer generally include, for example, polystyrene-co-butadiene, polystyrene-co-acrylonitrile, modified acrylic polymers, polyvinyl acetate, styrene-alkyd resins, soya-alkyl resins, polyvinylchloride, polyvinylidene chloride, polyacrylonitrile, polycarbonates, polyacrylic acid, polyacrylates, polymethacrylates, styrene polymers, polyvinyl butyral, alkyd resins, polyamides, polyurethanes, polyesters, polysulfones, polyethers, polyketones, phenoxy resins, epoxy resins, silicone resins, polysiloxanes, poly(hydroxyether) resins, polyhydroxystyrene resins, novolak, poly(phenylglycidyl ether)-co-dicyclopentadiene, copolymers of monomers used in the above-mentioned polymers, and combinations thereof. Specific suitable binders include, for example, polyvinyl butyral, polycarbonate, and polyester. Non-limiting examples of polyvinyl butyral include BX-1 and BX-5 from Sekisui Chemical Co. Ltd., Japan. Non-limiting examples of suitable polycarbonate include polycarbonate A which is derived from bisphenol-A (e.g. Iupilon-A from Mitsubishi Engineering Plastics, or Lexan 145 from General Electric); polycarbonate Z which is derived from cyclohexylidene bisphenol (e.g. Iupilon-Z from Mitsubishi Engineering Plastics Corp, White Plain, New York); and polycarbonate C which is derived from methylbisphenol A (from Mitsubishi Chemical Corporation). Non-limiting examples of suitable polyester binders include ortho-polyethylene terephthalate (e.g. OPET TR-4 from Kanebo Ltd., Yamaguchi, Japan).

Suitable optional additives for any one or more of the layers include, for example, antioxidants, coupling agents, dispersing agents, curing agents, surfactants, and combinations thereof.

5 The photoconductive element overall typically has a thickness from about 10 microns to about 45 microns. In the dual layer embodiments having a separate charge generating layer and a separate charge transport layer, charge generation layer generally has a thickness from about 0.5 microns to about 2 microns, and the charge transport layer has a thickness from about 5 microns to about 35 microns. In embodiments in which the charge transport material and the charge generating compound are in the same layer, the  
10 layer with the charge generating compound and the charge transport composition generally has a thickness from about 7 microns to about 30 microns. In embodiments with a distinct electron transport layer, the electron transport layer has an average thickness from about 0.5 microns to about 10 microns and in further embodiments from about 1 micron to about 3 microns. In general, an electron transport overcoat layer can  
15 increase mechanical abrasion resistance, increases resistance to carrier liquid and atmospheric moisture, and decreases degradation of the photoreceptor by corona gases. A person of ordinary skill in the art will recognize that additional ranges of thickness within the explicit ranges above are contemplated and are within the present disclosure.

Generally, for the organophotoreceptors described herein, the charge generation  
20 compound is in an amount from about 0.5 to about 25 weight percent, in further embodiments in an amount from about 1 to about 15 weight percent, and in other embodiments in an amount from about 2 to about 10 weight percent, based on the weight of the photoconductive layer. The charge transport material is in an amount from about 10 to about 80 weight percent, based on the weight of the photoconductive layer, in  
25 further embodiments in an amount from about 35 to about 60 weight percent, and in other embodiments from about 45 to about 55 weight percent, based on the weight of the photoconductive layer. The optional second charge transport material, when present, can be in an amount of at least about 2 weight percent, in other embodiments from about 2.5 to about 25 weight percent, based on the weight of the photoconductive layer, and in  
30 further embodiments in an amount from about 4 to about 20 weight percent, based on the weight of the photoconductive layer. The binder is in an amount from about 15 to about

80 weight percent, based on the weight of the photoconductive layer, and in further embodiments in an amount from about 20 to about 75 weight percent, based on the weight of the photoconductive layer. A person of ordinary skill in the art will recognize that additional ranges within the explicit ranges of compositions are contemplated and are  
5 within the present disclosure.

For the dual layer embodiments with a separate charge generating layer and a charge transport layer, the charge generation layer generally comprises a binder in an amount from about 10 to about 90 weight percent, in further embodiments from about 15 to about 80 weight percent and in some embodiments in an amount from about 20 to  
10 about 75 weight percent, based on the weight of the charge generation layer. The optional charge transport material in the charge generating layer, if present, generally can be in an amount of at least about 2.5 weight percent, in further embodiments from about 4 to about 30 weight percent and in other embodiments in an amount from about 10 to about 25 weight percent, based on the weight of the charge generating layer. The charge  
15 transport layer generally comprises a binder in an amount from about 20 weight percent to about 70 weight percent and in further embodiments in an amount from about 30 weight percent to about 50 weight percent. A person of ordinary skill in the art will recognize that additional ranges of binder concentrations for the dual layer embodiments within the explicit ranges above are contemplated and are within the present disclosure.

For the embodiments with a single layer having a charge generating compound and a charge transport material, the photoconductive layer generally comprises a binder, a charge transport material, and a charge generation compound. The charge generation compound can be in an amount from about 0.05 to about 25 weight percent and in further embodiment in an amount from about 2 to about 15 weight percent, based on the weight  
25 of the photoconductive layer. The charge transport material can be in an amount from about 10 to about 80 weight percent, in other embodiments from about 25 to about 65 weight percent, in additional embodiments from about 30 to about 60 weight percent and in further embodiments in an amount from about 35 to about 55 weight percent, based on the weight of the photoconductive layer, with the remainder of the photoconductive layer comprising the binder, and optionally additives, such as any conventional additives. A  
30 single layer with a charge transport composition and a charge generating compound

generally comprises a binder in an amount from about 10 weight percent to about 75 weight percent, in other embodiments from about 20 weight percent to about 60 weight percent, and in further embodiments from about 25 weight percent to about 50 weight percent. Optionally, the layer with the charge generating compound and the charge transport material may comprise a second charge transport material. The optional second charge transport material, if present, generally can be in an amount of at least about 2.5 weight percent, in further embodiments from about 4 to about 30 weight percent and in other embodiments in an amount from about 10 to about 25 weight percent, based on the weight of the photoconductive layer. A person of ordinary skill in the art will recognize that additional composition ranges within the explicit compositions ranges for the layers above are contemplated and are within the present disclosure.

In general, any layer with an electron transport layer can advantageously further include a UV light stabilizer. In particular, the electron transport layer generally can comprise an electron transport compound, a binder, and an optional UV light stabilizer. An overcoat layer comprising an electron transport compound is described further in copending U.S. Patent Application Serial No. 10/396,536 to Zhu et al. entitled, "Organophotoreceptor With An Electron Transport Layer," incorporated herein by reference. For example, an electron transport compound as described above may be used in the release layer of the photoconductors described herein. The electron transport compound in an electron transport layer can be in an amount from about 10 to about 50 weight percent, and in other embodiments in an amount from about 20 to about 40 weight percent, based on the weight of the electron transport layer. A person of ordinary skill in the art will recognize that additional ranges of compositions within the explicit ranges are contemplated and are within the present disclosure.

The UV light stabilizer, if present, in any one or more appropriate layers of the photoconductor generally is in an amount from about 0.5 to about 25 weight percent and in some embodiments in an amount from about 1 to about 10 weight percent, based on the weight of the particular layer. A person of ordinary skill in the art will recognize that additional ranges of compositions within the explicit ranges are contemplated and are within the present disclosure.

For example, the photoconductive layer may be formed by dispersing or dissolving the components, such as one or more of a charge generating compound, the charge transport material of this invention, a second charge transport material such as a charge transport compound or an electron transport compound, a UV light stabilizer, and  
5 a polymeric binder in organic solvent, coating the dispersion and/or solution on the respective underlying layer and drying the coating. In particular, the components can be dispersed by high shear homogenization, ball-milling, attritor milling, high energy bead (sand) milling or other size reduction processes or mixing means known in the art for effecting particle size reduction in forming a dispersion.

10 The photoreceptor may optionally have one or more additional layers as well. An additional layer can be, for example, a sub-layer or an overcoat layer, such as a barrier layer, a release layer, a protective layer, or an adhesive layer. A release layer or a protective layer may form the uppermost layer of the photoconductor element. A barrier layer may be sandwiched between the release layer and the photoconductive element or  
15 used to overcoat the photoconductive element. The barrier layer provides protection from abrasion to the underlayers. An adhesive layer locates and improves the adhesion between a photoconductive element, a barrier layer and a release layer, or any combination thereof. A sub-layer is a charge blocking layer and locates between the electrically conductive substrate and the photoconductive element. The sub-layer may  
20 also improve the adhesion between the electrically conductive substrate and the photoconductive element.

Suitable barrier layers include, for example, coatings such as crosslinkable siloxanol-colloidal silica coating and hydroxylated silsesquioxane-colloidal silica coating, and organic binders such as polyvinyl alcohol, methyl vinyl ether/maleic anhydride  
25 copolymer, casein, polyvinyl pyrrolidone, polyacrylic acid, gelatin, starch, polyurethanes, polyimides, polyesters, polyamides, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polycarbonates, polyvinyl butyral, polyvinyl acetoacetal, polyvinyl formal, polyacrylonitrile, polymethyl methacrylate, polyacrylates, polyvinyl carbazoles, copolymers of monomers used in the above-mentioned polymers, vinyl chloride/vinyl  
30 acetate/vinyl alcohol terpolymers, vinyl chloride/vinyl acetate/maleic acid terpolymers, ethylene/vinyl acetate copolymers, vinyl chloride/vinylidene chloride copolymers,

cellulose polymers, and mixtures thereof. The above barrier layer polymers optionally may contain small inorganic particles such as fumed silica, silica, titania, alumina, zirconia, or a combination thereof. Barrier layers are described further in U.S. Patent 6,001,522 to Woo et al., entitled "Barrier Layer For Photoconductor Elements  
5 Comprising An Organic Polymer And Silica," incorporated herein by reference. The release layer topcoat may comprise any release layer composition known in the art. In some embodiments, the release layer is a fluorinated polymer, siloxane polymer, fluorosilicone polymer, silane, polyethylene, polypropylene, polyacrylate, or a combination thereof. The release layers can comprise crosslinked polymers.

10 The release layer may comprise, for example, any release layer composition known in the art. In some embodiments, the release layer comprises a fluorinated polymer, siloxane polymer, fluorosilicone polymer, polysilane, polyethylene, polypropylene, polyacrylate, poly(methyl methacrylate-co-methacrylic acid), urethane resins, urethane-epoxy resins, acrylated-urethane resins, urethane-acrylic resins, or a  
15 combination thereof. In further embodiments, the release layers comprise crosslinked polymers.

The protective layer can protect the organophotoreceptor from chemical and mechanical degradation. The protective layer may comprise any protective layer composition known in the art. In some embodiments, the protective layer is a fluorinated  
20 polymer, siloxane polymer, fluorosilicone polymer, polysilane, polyethylene, polypropylene, polyacrylate, poly(methyl methacrylate-co-methacrylic acid), urethane resins, urethane-epoxy resins, acrylated-urethane resins, urethane-acrylic resins, or a combination thereof. In some embodiments of particular interest, the release layers are crosslinked polymers.

25 An overcoat layer may comprise an electron transport compound as described further in copending U.S. Patent Application Serial No. 10/396,536, filed on March 25, 2003 to Zhu et al. entitled, "Organoreceptor With An Electron Transport Layer," incorporated herein by reference. For example, an electron transport compound, as described above, may be used in the release layer of this invention. The electron  
30 transport compound in the overcoat layer can be in an amount from about 2 to about 50 weight percent, and in other embodiments in an amount from about 10 to about 40 weight

percent, based on the weight of the release layer. A person of ordinary skill in the art will recognize that additional ranges of composition within the explicit ranges are contemplated and are within the present disclosure.

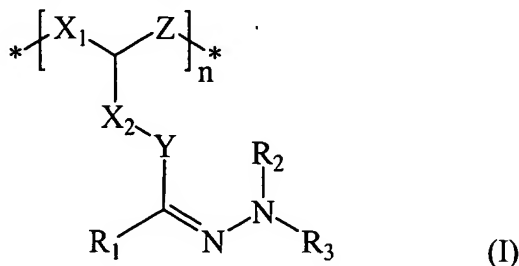
Generally, adhesive layers comprise a film forming polymer, such as polyester,  
5 polyvinylbutyral, polyvinylpyrrolidone, polyurethane, polymethyl methacrylate, poly(hydroxy amino ether) and the like. Barrier and adhesive layers are described further in U.S. Patent 6,180,305 to Ackley et al., entitled "Organic Photoreceptors for Liquid Electrophotography," incorporated herein by reference.

Sub-layers can comprise, for example, polyvinylbutyral, organosilanes,  
10 hydrolyzable silanes, epoxy resins, polyesters, polyamides, polyurethanes, cellulose, and the like. In some embodiments, the sub-layer has a dry thickness between about 20 Angstroms and about 20,000 Angstroms. Sublayers containing metal oxide conductive particles can be between about 1 and about 25 microns thick. A person of ordinary skill in the art will recognize that additional ranges of compositions and thickness within the  
15 explicit ranges are contemplated and are within the present disclosure.

The charge transport materials as described herein, and photoreceptors including these compounds, are suitable for use in an imaging process with either dry or liquid toner development. For example, any dry toners and liquid toners known in the art may be used in the process and the apparatus of this invention. Liquid toner development can  
20 be desirable because it offers the advantages of providing higher resolution images and requiring lower energy for image fixing compared to dry toners. Examples of suitable liquid toners are known in the art. Liquid toners generally comprise toner particles dispersed in a carrier liquid. The toner particles can comprise a colorant/pigment, a resin binder, and/or a charge director. In some embodiments of liquid toner, a resin to pigment  
25 ratio can be from 1:1 to 10:1, and in other embodiments, from 4:1 to 8:1. Liquid toners are described further in Published U.S. Patent Applications 2002/0128349, entitled "Liquid Inks Comprising A Stable Organosol," and 2002/0086916, entitled "Liquid Inks Comprising Treated Colorant Particles," and U.S. Patent No. 6,649,316, entitled "Phase Change Developer For Liquid Electrophotography," all three of which are incorporated  
30 herein by reference.

## Charge Transport Material

As described herein, an organophotoreceptor comprises a charge transport material comprising a polymer having the formula



where  $X_1$  and  $X_2$  are, each independently, a bond or a linking group, such as a  $-(CH_2)_m-$  group, where  $m$  is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, an  $NR_a$  group, a  $CR_b$  group, a  $CR_cR_d$  group, or a  $SiR_eR_f$  where  $R_a$ ,  $R_b$ ,  $R_c$ ,  $R_d$ ,  $R_e$ , and  $R_f$  are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, an alkyl group, an alkoxy group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups or a benzo group;

Y comprises a bond or an arylamine group, such as carbazolyl groups and (N-substituted)arylamine groups;

Z comprises a bond, O, S, or NR<sub>4</sub>;

R<sub>1</sub> and R<sub>4</sub> comprise, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group;

R<sub>2</sub> and R<sub>3</sub> comprise, each independently, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group; and

$n$  is a distribution of integers between 1 and 100,000 with an average value of greater than one.

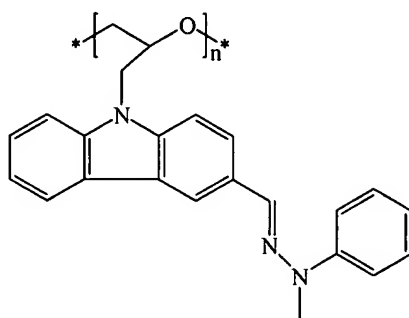
When Y is a carbazolyl group, Y may be an N-carbazolyl group where the N atom of the carbazolyl ring is bonded to the X<sub>2</sub> directly, or a C-carbazolyl group where one of the carbon atoms in the carbazolyl ring is bonded to the X<sub>2</sub> directly. When Y is an arylamine group, X<sub>2</sub> is bonded to the N atom of the arylamine group. In some embodiments, Y is an (N-substituted)arylamine group. In other embodiments, X<sub>1</sub> and X<sub>2</sub>



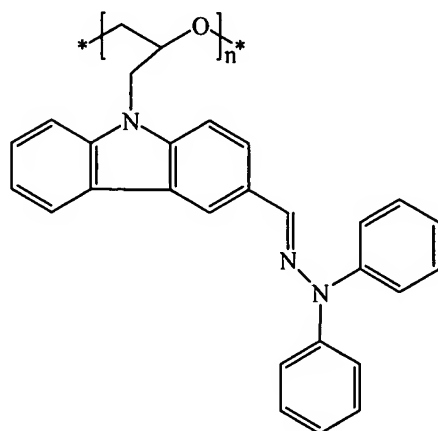
are, each independently, a bond or a  $-(CH_2)_m-$  group. In further embodiments,  $X_1$  and  $X_2$  are, each independently, a bond or a  $-CH_2-$  group; and Z is O or S.

With respect to Formula (I), substitution is liberally allowed, especially on  $X_1$ ,  $X_2$ , Y, and Z. Variation of the substituents, such as an aromatic group, an alkyl group, a heterocyclic group, and a ring group such as a benzo group, on  $X_1$ , and  $X_2$ , Y, and Z can result in various physical effects on the properties of the compounds, such as mobility, solubility, compatibility, stability, spectral absorbance, dispersibility, and the like, including, for example, substitutions known in the art to effect particular modifications.

In some embodiments, the organophotoreceptors as described herein can comprise an improved charge transport material of Formula (I) where  $X_1$  and  $X_2$  are, each independently, a bond or a  $-CH_2-$  group; Z is O; and Y is an N-carbazolyl group. Specific, non-limiting examples of suitable charge transport materials within Formula (I) of the present invention have the following structures:



(1) and

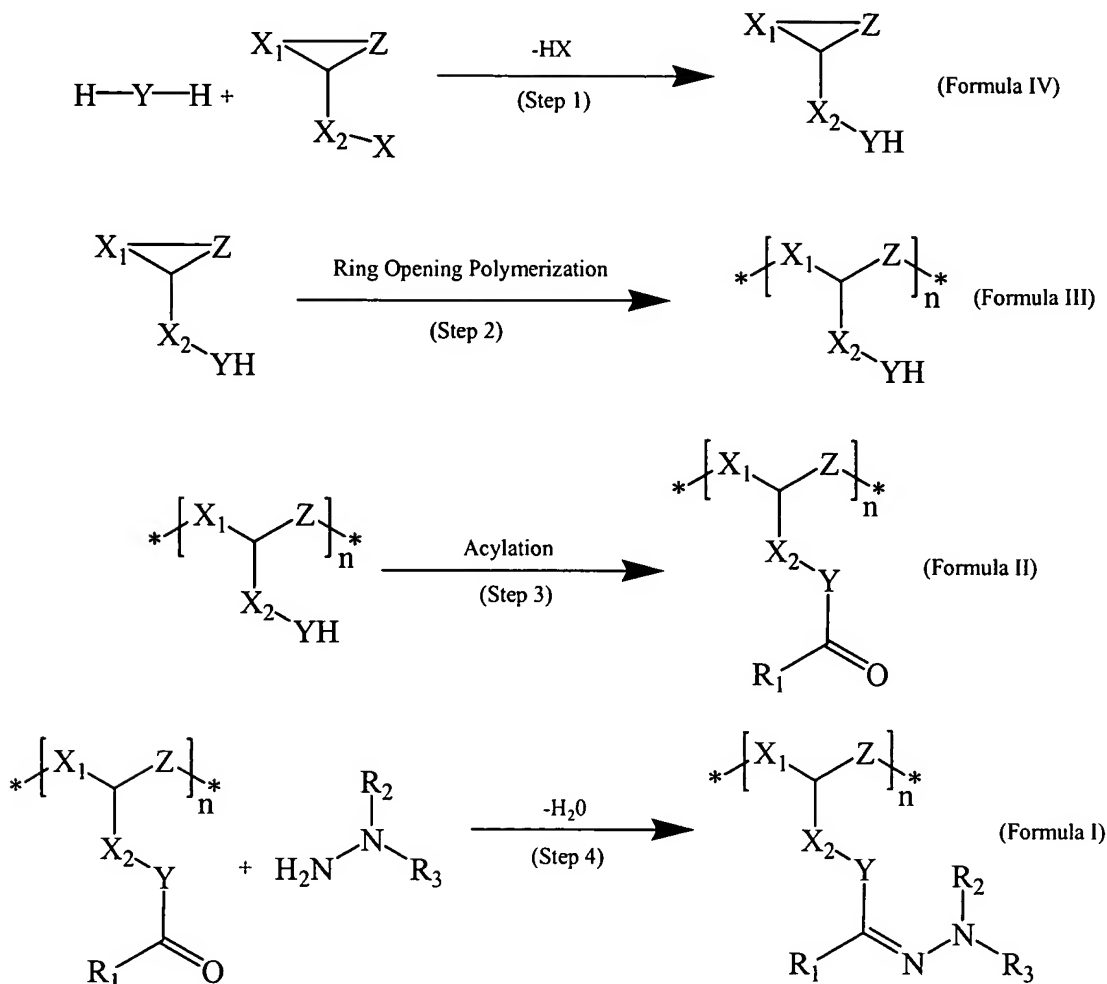


(2).

Synthesis Of Charge Transport Materials

The synthesis of the charge transport materials of this invention can be prepared by the following multi-step synthetic procedures A-D, although other suitable synthetic procedures can be used by a person of ordinary skill in the art based on the disclosure  
 5 herein.

The letter groups in the structures in Procedures A-D below are defined as followings.  $X_1$  and  $X_2$  are, each independently, a bond or a linking group, such as a  $-(CH_2)_m-$  group, where  $m$  is an integer between 1 and 10, inclusive, and one or more of the methylene groups is optionally replaced by O, S, N, C, B, Si, P, C=O, O=S=O, an  
 10  $NR_a$  group, a  $CR_b$  group, a  $CR_cR_d$  group, or a  $SiR_eR_f$  where  $R_a$ ,  $R_b$ ,  $R_c$ ,  $R_d$ ,  $R_e$ , and  $R_f$  are, each independently, a bond, H, a hydroxyl group, a thiol group, a carboxyl group, an amino group, an alkyl group, an alkoxy group, an alkenyl group, an alkynyl group, a heterocyclic group, an aromatic group, or a part of a ring group, such as cycloalkyl groups or a benzo group. Y comprises a bond or an arylamine group, such as a carbazolyl  
 15 group and (N-substituted)arylamine. Z comprises a bond, O, S, or  $NR_4$ .  $R_1$  and  $R_4$  comprise, each independently, H, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group.  $R_2$  and  $R_3$  comprise, each independently, an alkyl group, an alkenyl group, an alkynyl group, an aromatic group, or a heterocyclic group. The term  $n$  is a distribution of integers between 1 and 100,000 with an average  
 20 value of greater than one.

General Synthetic Procedure A

The first step of Procedure A is the formation of a reactive ring compound of Formula (IV) by reacting a suitable arylamine with an organic halide containing one reactive ring group, such as an epoxy group, a thiiranyl group, and an aziridino group.

The reactive ring group may be selected from the group consisting of heterocyclic ring groups which have a higher strain energy than its corresponding open-ring structure. The conventional definition of strain energy is that it represents the difference in energy between the actual molecule and a completely strain-free molecule of the same constitution. More information about the origin of strain energy can be found in the article by Wiberg et al., "A Theoretical Analysis of Hydrocarbon Properties: II Additivity of Group Properties and the Origin of Strain Energy," J. Am. Chem. Soc. **109**, 985 (1987). The above article is incorporated herein by reference. The heterocyclic ring group may

have 3, 4, 5, 7, 8, 9, 10, 11, or 12 members, in further embodiments 3, 4, 5, 7, or 8 members, in some embodiment 3, 4, or 8 members, and in additional embodiments 3 or 4 members. Non-limiting examples of such heterocyclic ring are cyclic ethers (e.g., epoxides and oxetane), cyclic amines (e.g., aziridine), cyclic sulfides (e.g., thiirane),  
5 cyclic amides (e.g., 2-azetidinone, 2-pyrrolidone, 2-piperidone, caprolactam, enantholactam, and capryllactam), N-carboxy- $\alpha$ -amino acid anhydrides, lactones, and cyclosiloxanes. The chemistry of the above heterocyclic rings is described in George Odian, "Principle of Polymerization," second edition, Chapter 7, p. 508-552 (1981), incorporated herein by reference.

10 In some embodiments of interest, the reactive ring group is an epoxy group. Non-limiting examples of suitable organic halide comprising an epoxy group as the reactive ring group are epihalohydrins, such as epichlorohydrin. The organic halide comprising an epoxy group can also be prepared by the epoxidation reaction of the corresponding alkene having a halide group. Such epoxidation reaction is described in Carey et al.,  
15 "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 494-498, incorporated herein by reference. The alkene having a halide group can be prepared by the Wittig reaction between a suitable aldehyde or keto compound and a suitable Wittig reagent. The Wittig and related reactions are described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp.  
20 69-77, which is incorporated herein by reference.

The various preparation procedures of epoxy compounds have been disclosed in U.S. Patent Application numbers 10/749,178, 10/634,164, 10/695,581, 10/663,970, and 10/692,389, and U.S. Provisional Patent Application numbers 60/444,001 and 60/459,150. All the above application references are incorporated herein by reference.

25 In some embodiments of interest, the reactive ring group is a thiiranyl group. An epoxy compound, such as those described above, can be converted into the corresponding thiiranyl compound by refluxing the epoxy compound and ammonium thiocyanate in tetrahydrofuran. Alternatively, the corresponding thiiranyl compound may be obtained by passing a solution of the above-described epoxy compound through 3-  
30 (thiocyano)propyl-functionalized silica gel (commercially available from Aldrich, Milwaukee, WI). Alternatively, a thiiranyl compound may be obtained by the thia-Payne

rearrangement of a corresponding epoxy compound. The thia-Payne rearrangement is described in Rayner, C. M. Synlett 1997, 11; Liu, Q. Y.; Marchington, A. P.; Rayner, C. M. Tetrahedron 1997, **53**, 15729; Ibuka, T. Chem. Soc. Rev. 1998, **27**, 145; and Rayner, C. M. Contemporary Organic Synthesis 1996, **3**, 499. All the above four articles are  
5 incorporated herein by reference.

In some embodiments of interest, the reactive ring group is an aziridinyl group. An aziridine compound may be obtained by the aza-Payne rearrangement of a corresponding epoxy compound, such as one of those epoxy compounds described above. The thia-Payne rearrangement is described in Rayner, C. M. Synlett 1997, 11; Liu, Q. Y.;  
10 Marchington, A. P.; Rayner, C. M. Tetrahedron 1997, **53**, 15729; and Ibuka, T. Chem. Soc. Rev. 1998, **27**, 145. All the above three articles are incorporated herein by reference. Alternatively, an aziridine compound may be prepared by the addition reaction between a suitable nitrene compound and a suitable alkene. Such addition reaction is described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York,  
15 1983, pp. 446-448, incorporated herein by reference.

In some embodiments of interest, the reactive ring group is an oxetanyl group. An oxetane compound may be prepared by the Paterno-Buchi reaction between a suitable carbonyl compound and a suitable alkene. The Paterno-Buchi reaction is described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York,  
20 1983, pp. 335-336, incorporated herein by reference.

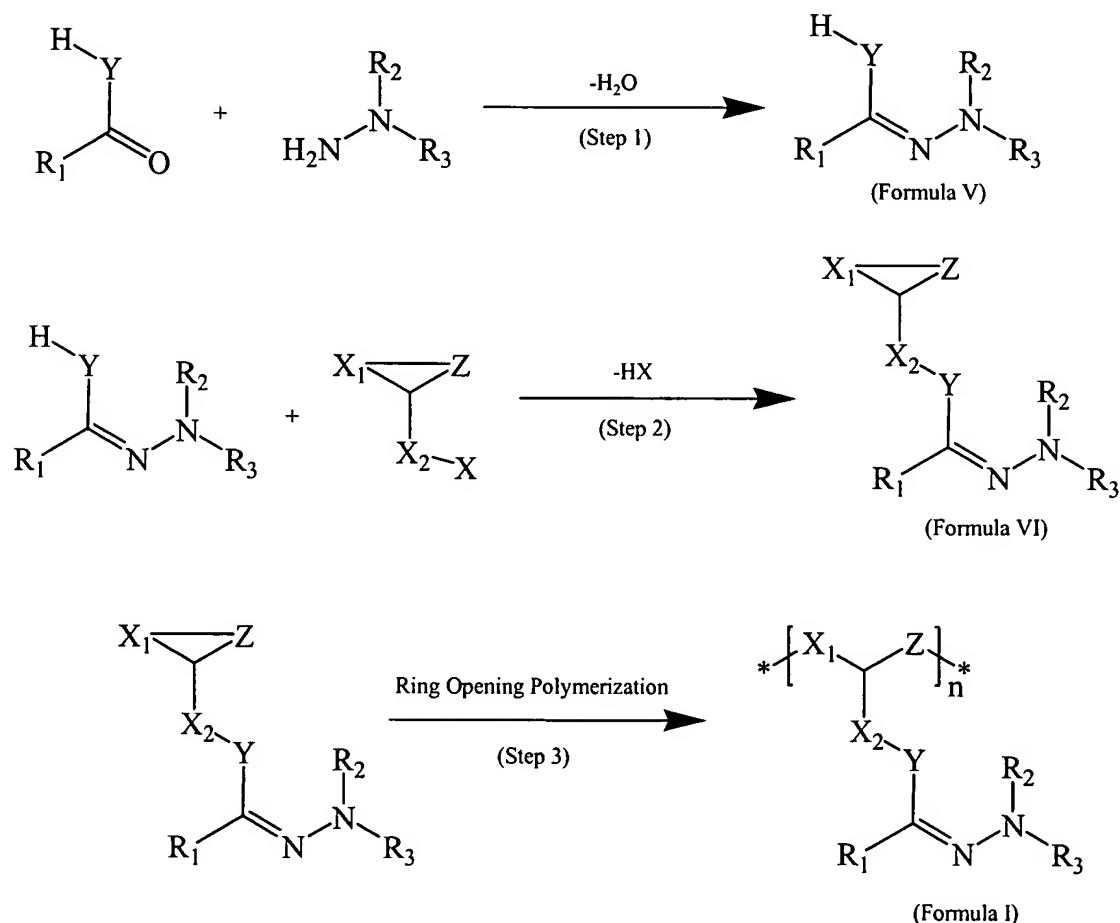
The second step is the ring opening polymerization of the reactive ring compound of Formula (IV) to form a polymer of Formula (III) having repeating arylamine groups. An initiator, such as protonic acids, Lewis acids, carbenium ions, oxonium ions, triethylaluminum, and diethylzinc, and a promoter, such as epihalohydrins, may be used  
25 for the ring opening polymerization. The ring opening polymerization reaction is described in the literature, such as in G. Odian, "Principles of Polymerization," 2nd Edition, Chapter 7, p. 508-565, which is incorporated herein by reference.

The third step is the acylation of the polymer of Formula (III) with a mixture of phosphorus oxychloride ( $\text{POCl}_3$ ) and a dialkylamide, such as N,N-dimethylformamide, to  
30 form a polymer of Formula (II) having repeating aldehyde or ketone group bonded to a carbazoyl group or an arylamine group. The Vilsmeier-Haack acylation and related

acylation reactions are described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 380-393, which is incorporated herein by reference. The order of Step 2 and Step 3 may be reversed, i.e., the acylation step may occur before the ring opening polymerization step.

- 5 The fourth step is the hydrazone formation by reacting an (N,N-disubstituted)hydrazine with the polymer of Formula (II) to form the charge transport material of Formula (I). The reaction can be catalyzed with an acid, such as sulfuric acid and hydrochloric acid.

# 10 General Synthetic Procedure B



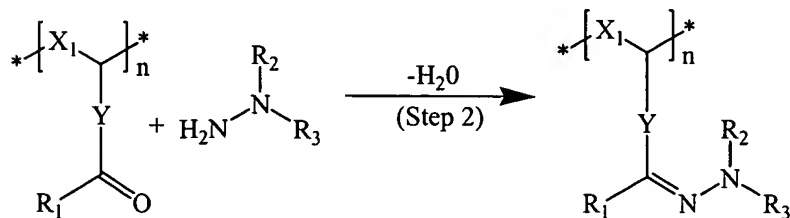
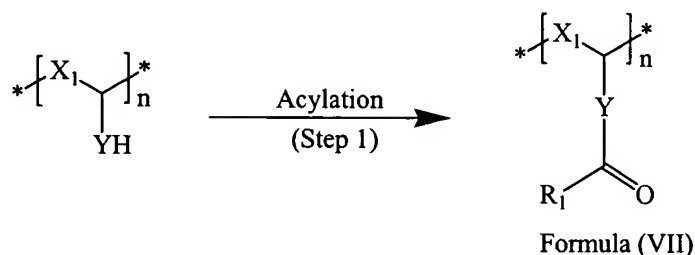
The first step of Procedure B is the hydrazone formation by reacting an arylamine having an aldehyde or a ketone group with an (N,N-disubstituted)hydrazine to form a

hydrazone of Formula (V). The reaction can be catalyzed with an acid, such as sulfuric acid and hydrochloric acid.

The second step is the formation of a reactive ring compound of Formula (VI) by reacting the hydrazone of Formula (V) with an organic halide containing one reactive ring group, such as an epoxy group, a thiiranyl group, or an aziridino group. The preparation of organic halides containing one reactive ring group has been disclosed above, which is incorporated herein by reference. In some embodiments, the organic halides comprising a reactive ring group are epihalohydrins, such as epichlorohydrin. The order of Step 1 and Step 2 may be reversed, i.e., a reactive ring compound may be formed before the formation of the hydrazone.

The third step is the ring opening polymerization of the reactive ring compound of Formula (VI) to form a charge transport material of Formula (I). An initiator, such as protonic acids, Lewis acids, carbenium ions, oxonium ions, triethylaluminum, and diethylzinc, and a promoter, such as epihalohydrins, may be used for the ring opening polymerization. The ring opening polymerization reaction is described in the literature, such as in G. Odian, "Principles of Polymerization," 2nd Edition, Chapter 7, p. 508-565, which is incorporated herein by reference.

### General Synthetic Procedure C



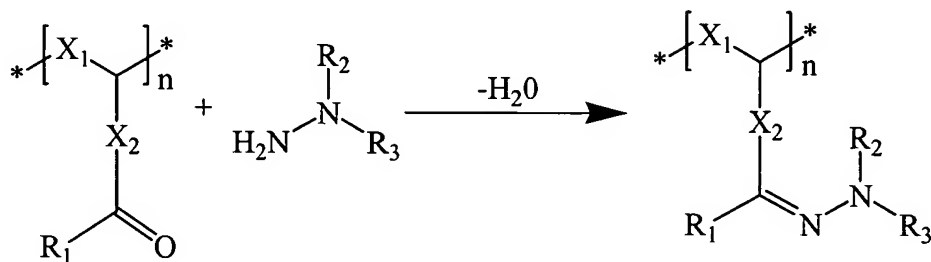
Formula (I) where X<sub>2</sub> and Z are a bond

The first step of procedure is the acylation of the arylamine groups in a polyvinyl polymer having repeating arylamine groups, such as poly(9-vinylcarbazole) which is

available from Aldrich, Milwaukee, WI, with a mixture of phosphorus oxychloride (POCl<sub>3</sub>) and a dialkylamide, such as N,N-dimethylformamide, to form a polymer of Formula (VII) having repeating aldehyde or ketone group bonded to an arylamine group, such as a carbazoyl group. The Vilsmeier-Haack acylation and related acylation reactions are described in Carey et al., "Advanced Organic Chemistry, Part B: Reactions and Synthesis," New York, 1983, pp. 380-393, which is incorporated herein by reference.

The second step is the hydrazone formation by reacting an (N,N-disubstituted)hydrazine with the polymer of Formula (VII) to form the charge transport material of Formula (I) where X<sub>2</sub> and Z are, each independently, a bond. In some embodiments, Y is an arylamine group, such as a carbazolyl group. The reaction can be catalyzed with an acid, such as sulfuric acid and hydrochloric acid.

#### General Synthetic Procedure D



Formula (I) where Y and Z are a bond

Procedure D requires only the hydrazone formation by reacting an (N,N-disubstituted)hydrazine with a polyvinyl polymer having a carbonyl group, such as poly(vinyl methyl ketone) which is available from ACROS Organics, Morris Plains, NJ, to form the charge transport material of Formula (I) where Y and Z are, each independently, a bond. In some embodiments, X<sub>2</sub> is a bond and R<sub>1</sub> may be an alkyl group or an aromatic group, such as an arylamine group including a carbazolyl group. In other embodiments, X<sub>2</sub> may be an -O-(CH<sub>2</sub>)<sub>k</sub>-O-Ar- group where Ar comprises an aromatic group and k is an integer between 1-10. The polyvinyl polymer having a carbonyl group and a X<sub>2</sub> group comprising an -O-(CH<sub>2</sub>)<sub>k</sub>-O-Ar- group may be prepared by the polymerization of the corresponding vinyl monomers having a carbonyl group and a X<sub>2</sub> group comprising an -O-(CH<sub>2</sub>)<sub>k</sub>-O-Ar- group. Such vinyl monomers are disclosed in the



literature, such as in Lee, et al., "Synthesis And Free Radical Polymerization Of Vinyl Ethers Containing Two Electron Acceptors," Bull. Korean Chem. Soc. 1999, Vol. 20, No. 11, p. 1355, which is incorporated herein by reference. The reaction can be catalyzed with an acid, such as sulfuric acid and hydrochloric acid.

5           The invention will now be described further by way of the following examples.

## EXAMPLES

### Example 1 - Synthesis And Characterization Charge Transport Materials

10           This example describes the synthesis and characterization of Compounds 1-2 in which the numbers refer to formula numbers above. The characterization involves chemical characterization of the compounds. The electrostatic characterization, such as mobility and ionization potential, of the materials formed with the compounds is presented in a subsequent example.

#### 15   Poly(9-(2,3-epoxypropyl)-3-formylcarbazole

          Dimethylformamide (DMF) (2.4 ml, 30.66 mmol, from Aldrich Chemicals, Milwaukee, WI) was added to a 25 ml, 3-neck round bottom flask equipped with a magnetic stirrer, a thermometer, and a dropping funnel. The flask and its content were cooled on a salted ice bath. When the temperature inside the flask reached 0 °C, 20   phosphorus oxychloride (POCl<sub>3</sub>, 2.8 ml, 30.66 mmol, obtained from Aldrich, Milwaukee, WI) was added slowly to the flask using a dropping funnel. During the addition of POCl<sub>3</sub>, the temperature inside the flask was kept at or below 5 °C. After the addition of POCl<sub>3</sub> was completed, the reaction mixture was allowed to warm to room temperature. Poly[9-(2,3-epoxypropyl)carbazole] (6.5 g, obtained from "Biolar", Rupnicu str. 3, Olaine LV- 25   2114, Latvia; Phone: +371 7964101, Fax: +371 7966555) in 7 ml of DMF was added to reaction mixture in the flask. After the reaction mixture was kept at 90 °C for 6 hours using a heating mantle, the reaction mixture was poured onto chopped ices and stirred manually with a stick. Then the mixture was neutralized with sodium acetate (obtained from Aldrich, Milwaukee, WI), stirred and cooled on an ice bath for 8 hours to yield the 30   product, poly(9-(2,3-epoxypropyl)-3-formylcarbazole), in the form of a solid precipitation. The product was filtered off, washed repeatedly with water and

subsequently with a small amount of isopropanol, and dried in a vacuum oven at 50 °C for 6 hours. The yield was 6.2 g (93 %). The IR spectrum of the product in a KBr salt window displayed the following characteristic vibrational frequencies,  $\nu$  (cm<sup>-1</sup>): 360-3220 (OH), 3050 (aromatic CH); and 2933, 2870, 2729 (aliphatic CH); 1685 (CHO); 905, 808, 766, 750, and 730 (carbazole).

#### Compound (1)

A mixture of [9-(2,3-epoxypropyl)-3-formylcarbazole] (1.5 g) and tetrahydrofuran (5 ml) was added to a 25 ml 3-neck round bottom flask equipped with a reflux condenser and a mechanical stirrer. The mixture was stirred at room temperature. After all solid entered into solution, N-methyl-N-phenylhydrazine (1.5 g, 12 mmol, obtained from Aldrich) was added to the mixture. The mixture was refluxed for approximately 2 hours and then cooled to room temperature. The mixture was filtered through a layer of silica gel (grade 62, 60-200 mesh, 150 Å) having a thickness of 3-4 cm and the silica gel was washed with tetrahydrofuran. A tetrahydrofuran solution was collected and concentrated to 5 ml by evaporation. The 5 ml concentrate was poured into 20-fold excess of hexane with intensive stirring. The resulting precipitate was filtered, washed repeatedly with 2-propanol, and dried in a vacuum oven at 50 °C for 5 hours. The yield of Compound (1) was 1.2 g (80 %). The IR spectrum of Compound (1) in a KBr salt window displayed the following characteristic vibrational frequencies,  $\nu$  (cm<sup>-1</sup>): 3590-3280 (OH), 3050 (aromatic CH); and 2930, 2874, 2810 (aliphatic CH); 902, 802, 748, and 692 (carbazole and monosubstituted benzene). The UV spectrum of Compound (1) in tetrahydrofuran was characterized by the following absorption wavelengths (nm, log  $\epsilon$ ): 208 (4.31); 242 (4.40); 310 (4.20); and 343 (4.37).

#### Compound (2)

A mixture of [9-(2,3-epoxypropyl)-3-formylcarbazole] (1.5 g) and tetrahydrofuran (5 ml) was added to a 25 ml 3-neck round bottom flask equipped with a reflux condenser and a mechanical stirrer. The mixture was stirred at room temperature. After all solid entered into solution, N,N-diphenylhydrazine hydrochloride (2.8 g, 0.0123 mole, obtained from Aldrich) in ethanol was added to the mixture. The mixture was

refluxed for approximately 2 hours and then cooled to room temperature. The mixture was filtered through a layer of silica gel (grade 62, 60-200 mesh, 150 Å) having a thickness of 3-4 cm and the silica gel was washed with tetrahydrofuran. A tetrahydrofuran solution was collected and concentrated to 5 ml by evaporation. The 5 ml concentrate was poured into 20-fold excess of hexane with intensive stirring. The resulting precipitate was filtered, washed repeatedly with 2-propanol, and dried in a vacuum oven at 50 °C for 5 hours. The yield of Compound (2) was 1.1 g (73 %). The IR spectrum of Compound (2) in a KBr salt window displayed the following characteristic vibrational frequencies,  $\nu$  (cm<sup>-1</sup>): 3590-3250 (end OH), 3055 (aromatic CH); 2929, 2870 (aliphatic CH); 748, and 700 (carbazole and monosubstituted benzene). The UV spectrum of Compound (2) in tetrahydrofuran was characterized by the following absorption wavelengths (nm, log  $\epsilon$ ): 210 (4.44); 243 (4.39); 309 (4.18); and 347 (4.31).

#### Example 2 - Charge Mobility Measurements

This example describes the measurement of charge mobility and ionization potential for charge transport materials, specifically Compounds (1) - (2) above.

##### Sample 1

A mixture of 0.1 g of the Compound (1) and 0.1 g of polycarbonate Z was dissolved in 2 ml of tetrahydrofuran. The solution was coated on a polyester film with a conductive aluminum layer by a dip roller. After the coating was dried for 1 hour at 80 °C, a clear 10 µm thick layer was formed. The hole mobility of the sample was measured and the results are presented in Table 1.

##### Sample 2

Sample 2 was prepared and tested similarly as Sample 1, except Compound (2) replaced Compound (1).

##### Mobility Measurements

Each sample was corona charged positively up to a surface potential U and illuminated with 2 ns long nitrogen laser light pulse. The hole mobility  $\mu$  was determined

as described in Kalade et al., "Investigation of charge carrier transfer in electrophotographic layers of chalcogenide glasses," Proceeding IPCS 1994: The Physics and Chemistry of Imaging Systems, Rochester, NY, pp. 747-752, incorporated herein by reference. The hole mobility measurement was repeated with appropriate changes to the charging regime to charge the sample to different U values, which corresponded to different electric field strength inside the layer E. This dependence on electric field strength was approximated by the formula

$$\mu = \mu_0 e^{\alpha \sqrt{E}}$$

Here E is electric field strength,  $\mu_0$  is the zero field mobility and  $\alpha$  is Pool-Frenkel parameter. Table 1 lists the mobility characterizing parameters  $\mu_0$  and  $\alpha$  values and the mobility value at the  $6.4 \times 10^5$  V/cm field strength as determined by these measurements for the four samples.

Table 1

Sample	$\mu_0$ (cm <sup>2</sup> /V·s)	$\mu$ (cm <sup>2</sup> /V·s) at $6.4 \cdot 10^5$ V/cm	$\alpha$ (cm/V) <sup>0.5</sup>	Ionization Potential (eV)
Sample 1/ Compound (1)	-	-	-	5.43
Sample 2/ Compound (2)	$2.6 \times 10^{-12}$	$1.5 \times 10^{-9}$	~0.008	5.49

### Example 3 - Ionization Potential Measurements

This example describes the measurement of the ionization potential for the 2 charge transport materials described in Example 1.

To perform the ionization potential measurements, a thin layer of charge transport material about 0.5  $\mu$ m thickness was coated from a solution of 2 mg of charge transport material in 0.2 ml of tetrahydrofuran on a 20 cm<sup>2</sup> substrate surface. The substrate was an aluminized polyester film coated with a 0.4  $\mu$ m thick methylcellulose sub-layer.

Ionization potential was measured as described in Grigalevicius et al., "3,6-Di(N-diphenylamino)-9-phenylcarbazole and its methyl-substituted derivative as novel hole-

transporting amorphous molecular materials,” *Synthetic Metals* **128** (2002), p. 127-131, incorporated herein by reference. In particular, each sample was illuminated with monochromatic light from the quartz monochromator with a deuterium lamp source. The power of the incident light beam was  $2.5 \cdot 10^{-8}$  W. A negative voltage of  $-300$  V was  
5 supplied to the sample substrate. A counter-electrode with the  $4.5 \times 15$  mm<sup>2</sup> slit for illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of a BK2-16 type electrometer, working in the open input regime, for the photocurrent measurement. A  $10^{-15} - 10^{-12}$  amp photocurrent was flowing in the circuit under illumination. The photocurrent,  $I$ , was strongly dependent on  
10 the incident light photon energy  $h\nu$ . The  $I^{0.5} = f(h\nu)$  dependence was plotted. Usually, the dependence of the square root of photocurrent on incident light quanta energy is well described by linear relationship near the threshold (see references “Ionization Potential of Organic Pigment Film by Atmospheric Photoelectron Emission Analysis,” *Electrophotography*, 28, Nr. 4, p. 364 (1989) by E. Miyamoto, Y. Yamaguchi, and M.  
15 Yokoyama; and “Photoemission in Solids,” *Topics in Applied Physics*, **26**, 1-103 (1978) by M. Cordona and L. Ley, both of which are incorporated herein by reference). The linear part of this dependence was extrapolated to the  $h\nu$  axis, and the  $I_p$  value was determined as the photon energy at the interception point. The ionization potential measurement has an error of  $\pm 0.03$  eV. The ionization potential values are given in  
20 Table 1 above.

As understood by those skilled in the art, additional substitution, variation among substituents, and alternative methods of synthesis and use may be practiced within the scope and intent of the present disclosure of the invention. The embodiments above are intended to be illustrative and not limiting. Additional embodiments are within the claims.  
25 Although the present invention has been described with reference to particular embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.